



Response to the comment on unraveling the role of cobalt in the direct conversion of CO₂ to high-yield liquid fuels and lube oil, [Appl. Catal. B, 305, 121041 (2022)]

Dear Prof. Verykios,

I am pleased to submit a response to the Comment on “Unraveling the role of cobalt in the direct conversion of CO₂ to high-yield liquid fuels and lube base oil” by Jo et al., Appl. Catal., B 2022, 305, 121041 by Heuntae Jo, Muhammad Kashif Khan, Muhammad Irshad, Malik Waqar Arshad, Seok Ki Kim (Co-corresponding Author), Jaehoon Kim (Corresponding Author).

In the process of preparing the response to the comments, we have answered all of the concerns expressed by Dr. Fredric Menuier:

Comment 1: First and most significant, the assignment of most IR bands is incorrect. Fig. 1 compares the DRIFTS bands assigned to surface species by Jo et al.¹ (Fig. 1. A) and the gasphase spectra of CO₂ and H₂O recorded in a 2-m pathlength transmission IR gas-cell by us (Fig. 1. B). All the bands assigned to CO adsorbed on various cobalt species (Fig. 1. A.) are actually those of CO₂(g) (Fig. 1.B.). The (very) weak CO₂ bands next the main asymmetric stretching of ¹²C¹⁶O₂ at 2349 cm⁻¹ (with intensity saturated here), are due to energy transitions (notably between excited states that are more populated at high temperatures) of CO₂ isotopic variants (with ¹²C or ¹³C and ¹⁶O, ¹⁷O or ¹⁸O). The details of more than five hundreds CO₂ bands located between 400 and 10000 cm⁻¹ have been tabulated by Rothman et al.^{2,3,4}. The same conclusion can be drawn for the bands near 1000 cm⁻¹ assigned by Jo et al. 오투! 책갈피가 정의되어 있지 않습니다. to various methoxy and carbonates species (Fig. 1.A.), which are again actually associated with CO₂(g) (Fig. 1.B.). Note that the sharp band at 949 cm⁻¹ superimposed on that of CO₂ is specifically that of gas-phase C₂H₄.

Response: To confirm the Dr. Menuier's comment on the assignments of the CO₂ bands, we now collect CO₂ IR bands by flowing CO₂ gas over KBr powder in our DRIFT cell. The IR bands of CO₂ are compared with those of adsorbed CO₂ on the CMO catalyst and those collected during the CO₂ hydrogenation. As shown in Fig. R1A, the IR bands collected at the beginning of the H₂ flow was very similar to those of CO₂ adsorbed on KBr. Thus, the peaks at 2130, 2107, 2094, 2078, and 1934 cm⁻¹ can be assigned to the CO₂ adsorption, as Dr. Menuier correctly commented. In addition, the peaks in the region of 900–1100 cm⁻¹ can be assigned to gaseous CO₂.

However, because of adsorbed CO exhibits peaks in this IR region, we now carefully check the IR profiles. When the IR bands were normalized by the peak at 2078 cm⁻¹ (which is the major CO₂ combination band), difference between the IR band collected over KBr and those over the CMO catalyst can be observed (Fig. R1B); with increasing H₂ flow time to 60 min over the CMO catalyst, new peaks at 2033, 2042, and 2064 cm⁻¹ were observed. In addition, as the H₂ flow time further increased to 90 min, the peak at 2064 cm⁻¹ shifted to 2066 cm⁻¹. The appearance of new peaks can be further confirmed by the 1st derivatives of the IR bands (Fig. R1C). If there was no reaction occurred and only the

concentration of CO₂ in the DRIFT cell decreased progressively with increasing H₂ flow time, the intensity of the whole normalized profiles should have been identical. Thus, the new peaks at 2033, 2042, and 2064 cm⁻¹ that were observed after the 60 min-H₂ flow can be attributed to CO₂-reacted species, not the CO₂ combination bands. Based on the control experiment of gaseous CO and H₂O adsorption on KBr (Figs. R1D and R1E, respectively), the peaks at 2033, 2042, and 2064 cm⁻¹ do not correspond to roto-vibrational peaks of gaseous CO and adsorbed H₂O. We think that we can assign the peak at 2033 cm⁻¹ to the linearly adsorbed CO on the cobalt site [Nunez et al., CO Hydrogenation on Cobalt-Based Catalysts: Tin Poisoning Unravels CO in Hollow Sites as a Main Surface Intermediate, Angew. Chem., Int. Ed. 57 (2018) 547–550]. The peak shifting from 2064 to 2066 cm⁻¹ after the 90 min H₂ flow could be attributed to the adsorbed CO on cobalt carbide [Couple et al., Experimental Microkinetic Approach of the Surface Reconstruction of Cobalt Particles in Relationship with the CO/H₂ Reaction on a Reduced 10% Co/Al₂O₃ Catalyst, J. Phys. Chem. C. 117 (2013) 14544–14557]. However, because assignment of the CO-adsorbed peak could be controversial, we think that it is not appropriate to assign the peaks at 2033, 2042, and 2064 cm⁻¹. Based on the discussion thus far, we will prepare erratum to the paper; to correct the wrong peak assignments (CO adsorption bands → CO₂ combination bands), to update DRIFT profiles, and to add the new IR bands of the control experiment in the Supplementary data.

Comment 2: The numerous bands in the region 1800–1300 cm⁻¹ assigned by Jo et al. 오투! 책갈피가 정의되어 있지 않습니다. to various adsorbates (Fig. 1.A.) are actually those of the gas-phase rotovibrational spectrum of water (Fig. 1.B.)^{5,6}. This is especially obvious because these rotovibrational bands are very narrow, the full width at half height (FWHH) being about 9 cm⁻¹. In contrast, bands of truly adsorbed species are significantly larger, e.g. on ZrO₂ the FWHH of the band of adsorbed water⁷ at 1640 cm⁻¹ is about 44 cm⁻¹ and that of formate⁸ at 1575 cm⁻¹ is about 52 cm⁻¹. Therefore, it appears that the current DRIFTS analysis reported by Jo et al. 오투! 책갈피가 정의되어 있지 않습니다. cannot be used to support the presence of various cobalt carbonyls and other surface species (whether or not those are actually present), since these authors mostly monitored the gas-phase signals of CO₂ and water, which overwhelmed the signal of adsorbates.

Response: To confirm the peaks of adsorbed H₂O, we now collect IR bands of adsorbed H₂O on KBr powder, as shown in Fig. R2. As Dr. Menuier correctly commented, there are numerous narrow FWHM peaks in the region of 1800–1300 cm⁻¹, which are associated with gas-phase roto-vibration of water molecules.

However, when H₂ was introduced into the DRIFT cell that contained pre-CO₂ adsorbed CMO catalyst, the spectra became broad, which can be deconvoluted with several broad FWHM peaks. In addition, as the H₂

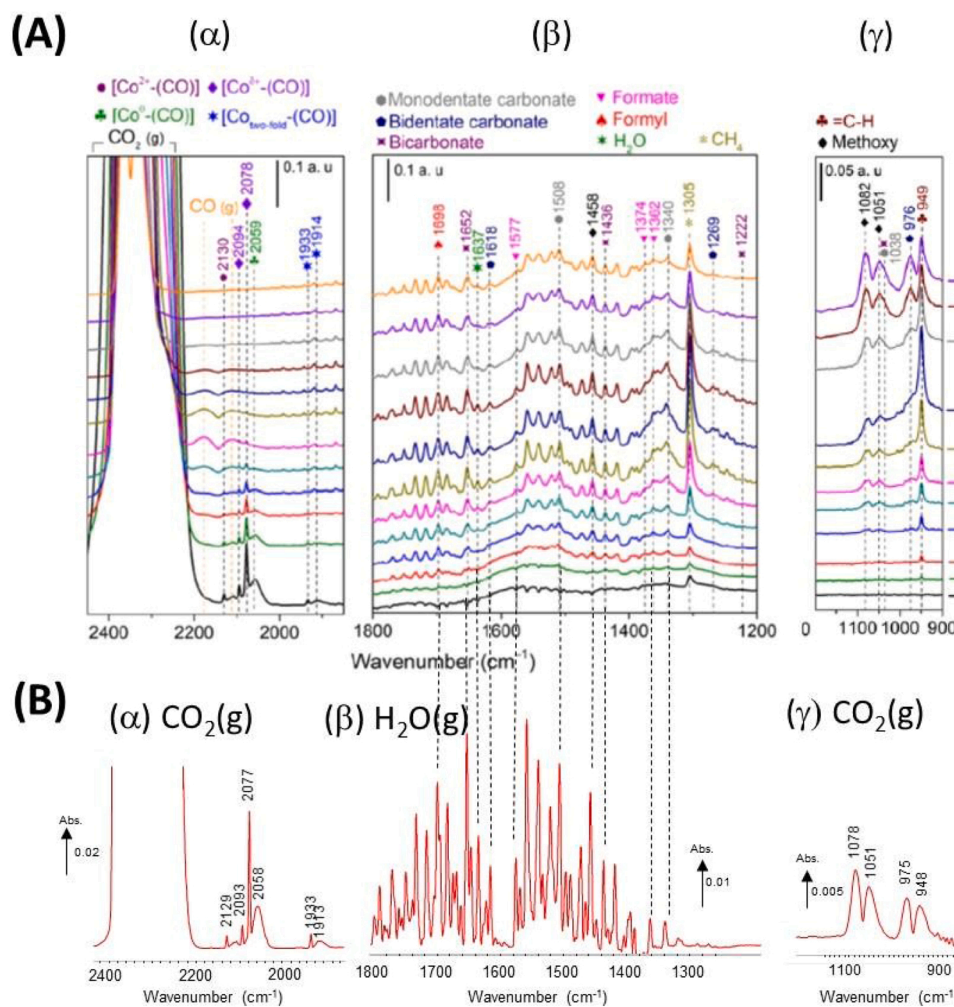


Fig. 1. Comparison of (A) *in situ* DRIFTS spectra reported in Figure 5 by Jo et al. in ref. [1] and (B) corresponding regions showing the IR gas-phase spectra of pure CO₂ and H₂O/He collected by the present authors at 80 °C in a 2 m-long IR gas-cell.

flow time increased, the intensity of the broad peaks increased. The peak associated with formates could be interfered by the H₂O peaks, but the intensity of the H₂O roto-vibrational peaks at 1400–1300 cm⁻¹ that were collected over the KBr powder are much weaker than those of formate. Therefore, we think that the broad FWHM peaks can be associated with mixed carbonate and formate species. However, because the peak deconvolution and fitting are rather tricky and debatable, we think that it is not appropriate to assign the peaks at 1800–1300 cm⁻¹ to each vibrational mode of carbonates and formates. In the erratum to the paper, the wrong peak assignments of carbonates, formates, and formyl will be corrected.

Comment 3: A second concern arises from the experimental conditions used in a spectroscopic cell (High-Temperature High-Pressure reaction cell from Harrick) that is renowned to exhibit major temperature control issues^{9,10}. The temperature of the top of the catalyst bed under Ar at atmospheric pressure was measured to be only 285 °C when that in the bed bulk was 350 °C¹⁰. The temperature of bed surfaces in most DRIFTS cells is typically lower than that expected (i) because the beds are heated underneath and (ii) because of the heat loss through the gas-mediated convective thermal contact between the bed and the cell dome, usually kept at room temperature. The temperature gradient is expected to be far greater if H₂ or He are used, because of the higher thermal conductivity of these gases. The pressure of 30 bars of pure H₂ used by Jo et al.¹ to reduce the cobalt catalyst at 350 °C would have led to a far lower temperature of the catalyst top layer, possibly preventing the reduction of cobalt oxides. This would explain the apparent lack of

Co⁰ carbonyl bands, that normally gives major IR signals in the 2060–1900 cm⁻¹ region^{11,12}.

Response: To check the temperature of the catalyst bed in the DRIFT cell, we now install a thermocouple on top of the catalyst bed (Fig. R3A). With increasing the temperature of heater at the bottom of the catalyst bed, the temperatures at the top of catalyst bed were recorded. As shown in Fig. R3B, when the temperature of heating block was 350 °C, the temperature at the top of catalyst bed was 270 °C. As shown in Fig. S36, partial reduction of Co₃O₄ could occur at this temperature. Although possibility of CO adsorption on metallic Co⁰ is excluded, CO could be adsorbed on the partially reduced Co⁺ [Kadinov et al., IR spectroscopy study of CO adsorption and of the interaction between CO and hydrogen on alumina-supported cobalt, J. Chem. Soc., Faraday Trans. 94 (1998) 3027–3031].

Comment 3: A third concern is the use of a highly KBr-diluted catalyst sample, using proportions 5:95. This would inevitably lead to a low signal coming from the catalyst and, especially, likely give rise to chemical or structural modifications of the sample by KBr, as already reported by Bianchi and co-workers¹³.

Response: We used the diluted catalyst sample because when we increased the black-colored catalyst amount, the signal-to-noise ratio of the DRIFT profile decreased; this could happen due to the reduction of reflection in the DRIFT cell at the high catalyst loading. Although we used the diluted catalyst sample, we think that the intensity of the peaks shown in Figs. R1A and R2 are enough to investigate *in situ* reaction behaviors.

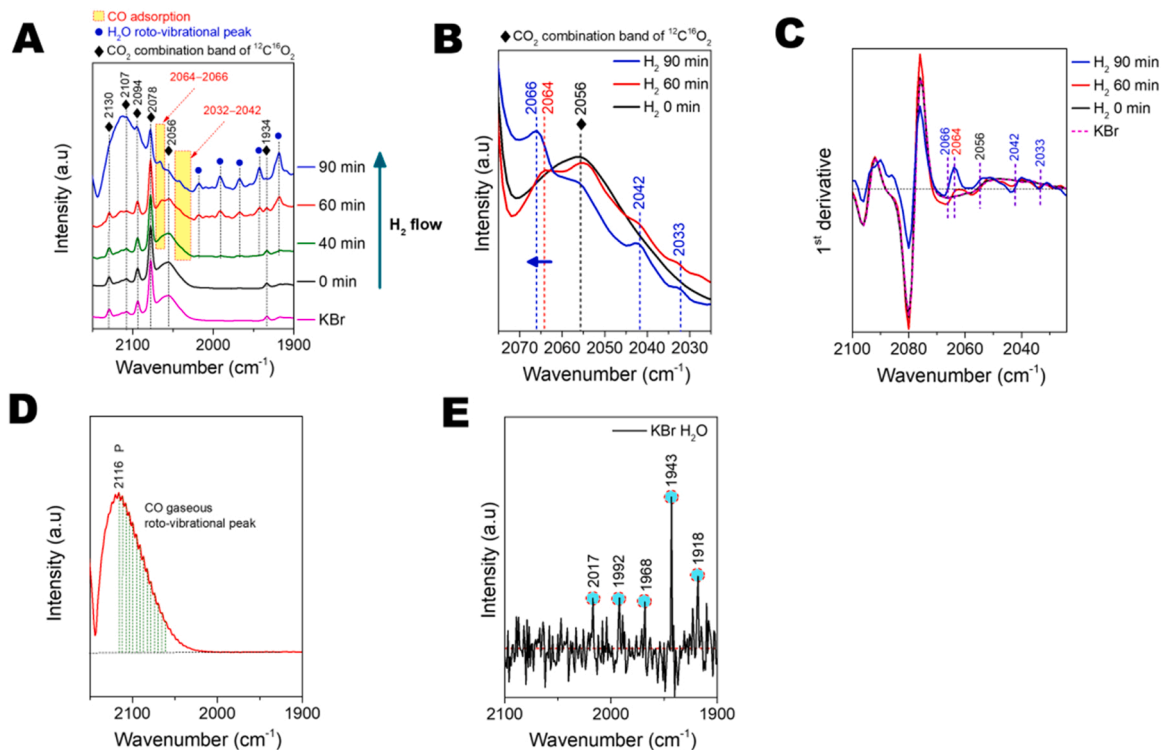


Fig. R1. (A) Comparison of IR bands that were collected during the CO₂ flow to the KBr containing DRIFT cell and during the H₂ flow to the pre-CO₂ adsorbed CMO catalyst containing DRIFT cell, (B) normalized IR bands, (C) the 1st derivatives of the IR bands, (D) gaseous CO roto-vibrational peaks, and (E) IR bands of water adsorption on KBr.

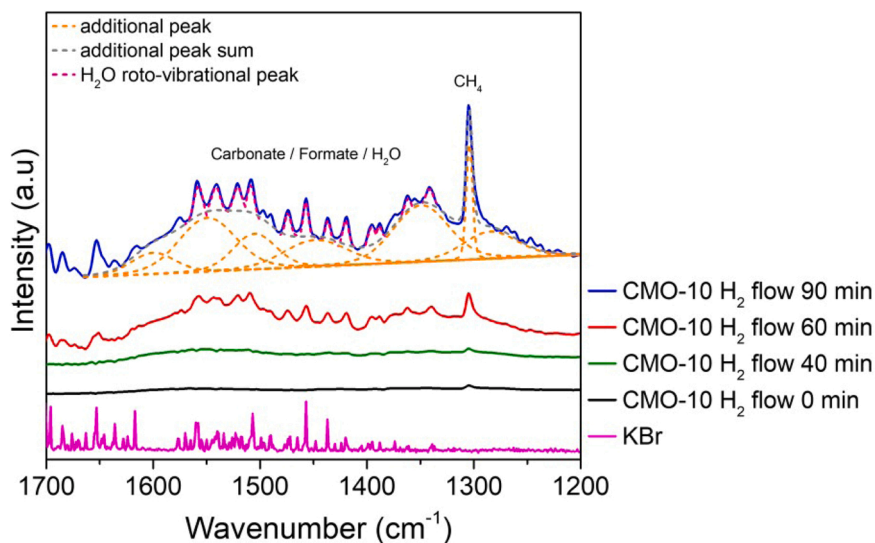


Fig. R2. The DRIFT profiles of adsorbed H₂O on KBr powder and those collected during the H₂ flow over the pre-CO₂ adsorbed CMO-10 catalyst.

Comment 4: In conclusion, we believe that the DRIFTS data reported in the paper by Jo et al. 오류! 책갈피가 정의되어 있지 않습니다. should be wholly reconsidered in view of the above-comments. We hope that these comments will provide a useful source of information to those using *in situ* and *operando* DRIFTS spectroscopy to investigate catalytic reactions, which is clearly not straightforward both on the experimental and data interpretation aspects, as discussed elsewhere 오류! 책갈피가 정의되어 있지 않습니다.,1.

Response: In an erratum to the paper, we will remove the peak assignments of CO adsorbed species and assign the peaks at 2100–1900 cm⁻¹ and 1200–900 cm⁻¹ to the combination band of

¹²C¹⁶O₂ (Fig. R4). In addition, the peaks at 1800–1300 cm⁻¹ will be assigned to carbonate/H₂O/formate, as shown in Fig. R4.

We believe that the corrections made to this manuscript at the suggestions of Dr. Menuier have made this a stronger paper and we thank you the reviewers for the help in this effort.

Please let us know if you need any additional information on this reply for the comments.

Sincerely yours,

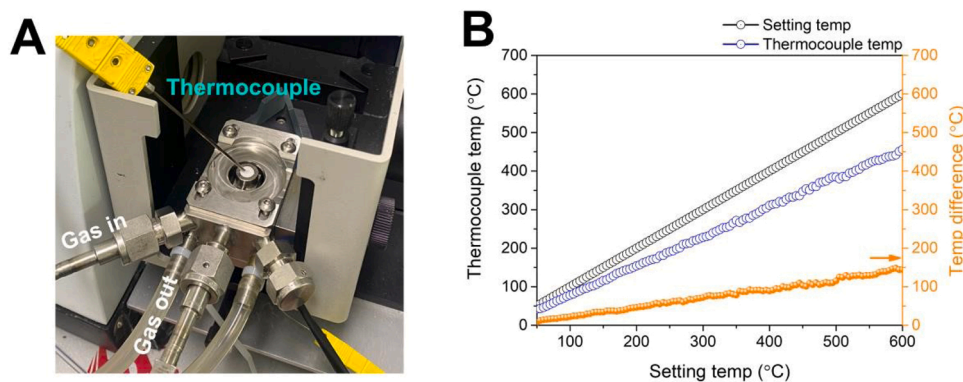


Fig. R3. DRIFT cell temperature test with thermocouple (A) and difference profile (B).

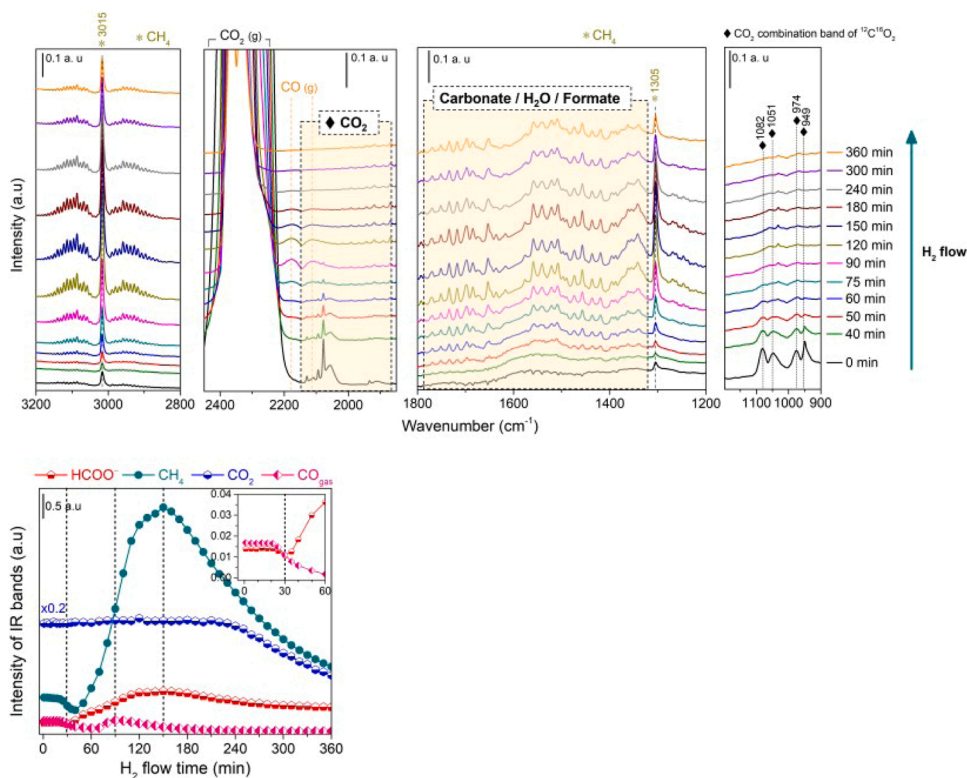


Fig. R4. Modified DRIFT profiles of CO₂ adsorption and H₂ flow profiles with CMO-10.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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